

NaSr₂CrF₈: A New Structure with Two "Independent F⁻"

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Received November 1, 1989

NaSr₂CrF₈ is monoclinic (space group $P2_1/c$) with $a = 7.7388(6)$ Å, $b = 6.2756(5)$ Å, $c = 14.827(2)$ Å, $\beta = 112.03(1)^\circ$, and $Z = 4$. The structure was solved from single crystal data using 2341 independent reflections ($R = 0.040$, $R_w = 0.043$). Chromium ions are in octahedral sites while two strontiums and one sodium atoms are respectively, in eight-, nine-, and sixfold coordination. The structure is characterized by isolated $[\text{CrF}_6]^{3-}$ octahedra between which sodium and strontium atoms and two independent fluorine ions are located. Cationic tetrahedra ($3\text{Sr}^{2+} + \text{Na}^+$) around independent fluorine ions form double chains, running in the [010] direction, with formula $[\text{F}_2\text{NaSr}_2]_n^{3n+}$. Structural correlations with CsCu₂Cl₃ are given. © 1990 Academic Press, Inc.

Introduction

During the past 10 years, we have studied fluorinated compounds in the ternary systems $\text{AF}-\text{MnF}_2-\text{MF}_3$ ($A = \text{Li}^+$ or Na^+ , $M =$ first row transition cations) in the scope to look at the magnetic behavior of crystal structures built up from octahedra sharing edges and (or) vertices (structural types: trirutile or Na_2SiF_6) (1-5). More recently our attention was focused on compounds belonging to the $\text{NaF}-\text{CaF}_2-\text{AlF}_3$ system (6, 7); the results obtained show that the Ca^{2+} ions can remain in sixfold coordination for compounds such as $\beta\text{-NaCaAlF}_6$ or $\text{Na}_4\text{Ca}_4\text{Al}_7\text{F}_{33}$ but that the eightfold coordination appears in $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$. Now we are studying ternary phases in the system $\text{NaF}-\text{SrF}_2-\text{CrF}_3$. Beside the large glassy domain previously described by J. P. Miranda (8) we find a new phase NaSrCrF_6 . In order to compare the cationic size radius effect on the deformation of the quasi hcp fluorine framework, crystal growth of this

phase was performed using a chloride flux technique. Beside the NaSrCrF_6 twinned crystals, other well-shaped green crystals were obtained. The good quality of these last crystals incited us to solve the structure. The $\text{NaSr}_2\text{CrF}_8$ formulation of this new compound was found from structure determination.

Preparation

Single crystals were grown, in a chloride flux (9, 10), by slow cooling ($5^\circ\text{C}/\text{hr}$) from 700°C of the mixture $\text{NaF} + \text{SrF}_2 + \text{CrF}_3 + 2.70\text{NaCl} + 1.65\text{ZnCl}_2$ in a platinum crucible under argon atmosphere. Two kinds of green crystals were isolated beside SrF_2 crystals. The first one, always twinned, was identified as NaSrCrF_6 (II) after X-ray powder diffraction analysis and the second one corresponded to a new phase, the formulation of which was determined as $\text{NaSr}_2\text{CrF}_8$ after structure resolution.

The thermal stability of $\text{NaSr}_2\text{CrF}_8$ stud-

TABLE I
CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION AND REFINEMENT FOR NaSr₂CrF₈

Symmetry	Monoclinic
Space group	<i>P2₁/c</i> (No. 14)
Cell parameters	<i>a</i> = 7.7388(6) Å, <i>b</i> = 6.2756(5) Å <i>c</i> = 14.827(2) Å, β = 112.03(1)° <i>V</i> = 667.48 Å ³ , <i>Z</i> = 4
Calculated density	4.00
Crystal volume (10 ⁻³ mm ³)	1.04
Radiation	MoKα (graphite monochromatized)
Detector aperture (mm)	3.5 × 3.5
Scanning mode	ω/2θ, time per step: 1–4 sec
Profile fitting data analysis (12)	Isotropic linewidth, ω = (0.75 + 0.30 tan θ) ²
Range registered	2θ _{min} –2θ _{max} : 3–70°; <i>hkl</i> _{max} : 12 10 23
Absorption correction	Gauss method, μ = 171.92 cm ⁻¹ <i>t</i> _{min} = 0.16, <i>t</i> _{max} = 0.48
Reflections measured: Total	4207
Independent	2795 (<i>R</i> _{average} = 0.046)
Used in refinement	2341 (<i>I</i> /σ(<i>I</i>) > 3)
Number of refined parameters	110
Weighting scheme	ω = 1/(σ ² (<i>F</i>) + 3.6 · 10 ⁻³ <i>F</i> ²)
Secondary extinction	ε = 4.4(3) × 10 ⁻⁷
Maximum height in final Fourier difference map	0.34 e ⁻ /Å ³

ied by DTA (NETSCH 404S; heating rate 300°C/hr) shows a transition point at 685(5)°C (not explained) and a decomposition point at 803(5)°C (for comparison the

melting point of NaSrCrF₆ is found at 828(5)°C.

NaSr₂CrF₈ powder synthesis attempts, in the solid state, from elementary fluorides

TABLE II
ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS (*U*_{*ij*} × 10⁴), AND *B*_{eq} (Å²) FOR NaSr₂CrF₈

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>B</i> _{eq} (Å ²)
Sr1	4e	0.09900(4)	0.27654(5)	0.19682(2)	99(1)	84(2)	90(2)	7(1)	40(1)	-3(1)	0.71(2)
Sr2	4e	0.41468(4)	0.84217(5)	0.35578(2)	81(1)	96(1)	85(1)	4(1)	39(1)	8(1)	0.67(1)
Cr	4e	0.69368(7)	0.27844(8)	0.40287(4)	96(2)	70(2)	60(2)	-2(1)	34(2)	-5(1)	0.58(2)
Na	4e	0.8553(3)	0.8234(3)	0.0585(1)	231(8)	201(8)	139(7)	42(6)	59(6)	22(6)	1.52(8)
F1	4e	0.1746(3)	0.8737(4)	0.1771(2)	139(8)	193(10)	97(8)	-5(7)	58(7)	32(7)	1.09(9)
F2 ^a	4e	0.8546(3)	0.5527(3)	0.1560(1)	107(7)	110(8)	110(8)	-1(7)	36(7)	-4(6)	0.87(8)
F3	4e	0.0824(3)	0.8014(4)	0.9848(2)	153(9)	169(10)	82(8)	-8(7)	22(7)	-2(7)	1.11(9)
F4 ^a	4e	0.8147(3)	0.0540(3)	0.1736(2)	130(8)	134(9)	116(8)	-3(7)	48(7)	7(7)	0.99(9)
F5	4e	0.6458(3)	0.9319(3)	0.9162(2)	186(9)	82(8)	189(10)	10(7)	12(8)	-42(7)	1.34(10)
F6	4e	0.5266(3)	0.7358(4)	0.2149(2)	117(9)	204(10)	106(9)	14(8)	29(7)	24(7)	1.15(10)
F7	4e	0.7456(3)	0.5147(3)	0.8898(2)	164(8)	81(8)	218(10)	48(7)	114(8)	-8(7)	1.12(10)
F8	4e	0.4531(3)	0.6880(4)	0.0280(2)	195(10)	189(10)	114(8)	-6(8)	97(7)	47(8)	1.22(10)

^a Independent fluorine.

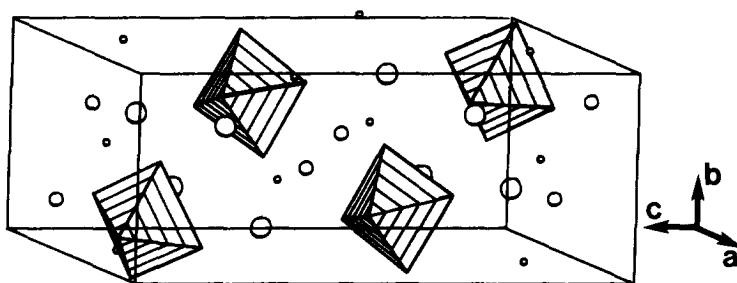


FIG. 1. Perspective view of $\text{NaSr}_2\text{CrF}_8$ (Sr, Na, F_{ind} , large, medium, and small circles, respectively).

have failed (with or without quenching for $650 < T < 800^\circ\text{C}$).

Nevertheless, in crystal growth the best results were performed with the following mixture: $\text{NaF} + 2\text{SrF}_2 + \text{CrF}_3 + 2.25\text{NaCl} + 2.75 \text{ZnCl}_2$ (775°C , slow cooling 4°C/hr , about a yield of 10% in $\text{NaSr}_2\text{CrF}_8$).

Structure Resolution

A crystal, with a truncated plate habit limited by many faces (101, 001, 010, 122, and the centered ones), was selected for X-ray data collection (Table I). The unit cell is monoclinic with lattice parameters— $a = 7.7388(6) \text{ \AA}$, $b = 6.2756(5) \text{ \AA}$, $c = 14.827(2) \text{ \AA}$, $\beta = 112.03(1)^\circ$ —refined from the positions of 28 reflections centered by the double scan technique (2θ , 30°). The limiting conditions for the reflections observed— $h0l$, $l = 2n$ and $0k0$, $k = 2n$ —are in agreement with the centric space group $P2_1/c$.

Intensities, corrected for Lorentz polarization effects as well as for absorption using the final composition, were averaged in the Laue group $2/m$ and led to a R_{av} value of 0.046. The structure was solved from fast automatic centrosymmetric direct methods, and refined using the SHELX-76 program (13). Ionic scattering factors and anomalous dispersion parameters were taken from International Tables for X-ray Crystallography (14).

Direct methods provided the location of

Sr, Cr, and Na atoms and successive Fourier difference maps and refinements revealed the position of all the fluorines. The final refinement with anisotropic thermal motion (Table II) dropped to $R = 0.040$ and $R_w = 0.043$ ($R = 0.071$ with isotropic thermal motion). Table III lists the main interatomic distances and angles. A table specifying the calculated and observed structure factors can be obtained upon request from the authors.

Structure Description and Discussion

The structure of $\text{NaSr}_2\text{CrF}_8$ can be considered as built up from isolated CrF_6 octahedra separated from each other by strontium (SrF_8 and SrF_9 polyhedra), sodium (NaF_6 polyhedra), and fluorine ions (Fig. 1).

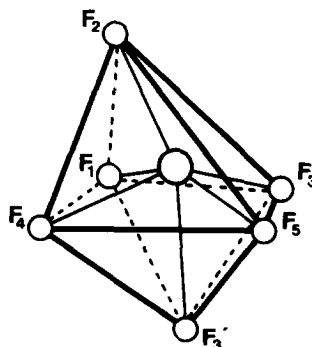


FIG. 2. Na polyhedron: sixfold coordination.

TABLE III
MAIN INTERATOMIC DISTANCES (Å) AND ANGLES (°)
IN NaSr₂CrF₈

Sr ₁ polyhedron [8]	Sr ₂ polyhedron [9]
Sr ₁ -F ₇ = 2.443(3)	Sr ₂ -F ₅ = 2.400(2)
Sr ₁ -F ₂ ^a = 2.468(2)	Sr ₂ -F ₂ ^a = 2.418(2)
Sr ₁ -F ₄ ^a = 2.492(2)	Sr ₂ -F ₄ ^a = 2.456(2)
Sr ₁ -F ₂ ^a = 2.505(2)	Sr ₂ -F ₈ = 2.464(3)
Sr ₁ -F ₄ ^a = 2.518(2)	Sr ₂ -F ₇ = 2.579(2)
Sr ₁ -F ₃ = 2.574(3)	Sr ₂ -F ₁ = 2.611(2)
Sr ₁ -F ₁ = 2.635(3)	Sr ₂ -F ₆ = 2.630(3)
Sr ₁ -F ₆ = 2.707(2)	Sr ₂ -F ₈ = 2.721(3)
(Sr ₁ -F) = 2.543	Sr ₂ -F ₆ = 2.786(2)
Sr-F _{theo} = 2.56	⟨Sr ₂ -F⟩ = 2.563
	Sr-F _{theo} = 2.61

Na polyhedron [6]

Na-F ₅ = 2.231(3)
Na-F ₂ ^a = 2.232(2)
Na-F ₄ ^a = 2.347(3)
Na-F ₃ = 2.396(4)
Na-F ₁ = 2.457(3)
Na-F ₃ ' = 2.534(3)
⟨Na-F⟩ = 2.366
Na-F _{theo} = 2.32

F ₅ -Na-F ₂ = 131.9(1)	F ₂ -Na-F ₃ ' = 156.7(1)
F ₅ -Na-F ₄ = 104.6(2)	F ₄ -Na-F ₃ = 133.5(1)
F ₅ -Na-F ₃ = 89.1(2)	F ₄ -Na-F ₁ = 76.9(2)
F ₅ -Na-F ₁ = 144.7(2)	F ₄ -Na-F ₃ ' = 72.6(2)
F ₅ -Na-F ₃ ' = 67.5(3)	F ₃ -Na-F ₁ = 67.7(2)
F ₂ -Na-F ₄ = 88.0(2)	F ₃ -Na-F ₃ ' = 72.3(2)
F ₂ -Na-F ₃ = 115.6(1)	F ₁ -Na-F ₃ ' = 80.0(2)
F ₂ -Na-F ₁ = 83.1(2)	

Cr octahedron

Cr-F ₈ = 1.880(3)
Cr-F ₅ = 1.880(3)
Cr-F ₃ = 1.906(3)
Cr-F ₇ = 1.908(3)
Cr-F ₁ = 1.926(3)
Cr-F ₆ = 1.948(3)
⟨Cr-F⟩ = 1.908
Cr-F _{theo} = 1.915

F ₈ -Cr-F ₅ = 92.9(2)	F ₅ -Cr-F ₆ = 94.9(2)
F ₈ -Cr-F ₃ = 94.8(2)	F ₃ -Cr-F ₇ = 90.3(2)
F ₈ -Cr-F ₇ = 87.6(2)	F ₃ -Cr-F ₁ = 89.8(2)
F ₈ -Cr-F ₁ = 175.3(1)	F ₃ -Cr-F ₆ = 175.5(2)
F ₈ -Cr-F ₆ = 86.7(2)	F ₇ -Cr-F ₁ = 93.2(2)
F ₅ -Cr-F ₃ = 89.2(2)	F ₇ -Cr-F ₆ = 85.6(2)
F ₅ -Cr-F ₇ = 179.3(3)	F ₁ -Cr-F ₆ = 88.7(2)
F ₅ -Cr-F ₁ = 86.3(2)	

TABLE III—Continued

F₂^a tetrahedron

F ₂ -Na = 2.232(3)	Na-F ₂ -Sr ₂ = 125.5(1)
F ₂ -Sr ₂ = 2.418(2)	Na-F ₂ -Sr ₁ = 120.4(1)
F ₂ -Sr ₁ = 2.468(2)	Na-F ₂ -Sr ₁ = 95.9(1)
F ₂ -Sr ₁ = 2.505(2)	Sr ₂ -F ₂ -Sr ₁ = 101.2(1)
⟨F ₂ -Na,Sr⟩ = 2.406	Sr ₂ -F ₂ -Sr ₁ = 102.0(1)
	Sr ₁ -F ₂ -Sr ₁ = 109.5(1)

F₄^a tetrahedron

F ₄ -Na = 2.347(3)	Na-F ₄ -Sr ₂ = 127.6(1)
F ₄ -Sr ₂ = 2.456(2)	Na-F ₄ -Sr ₁ = 93.4(1)
F ₄ -Sr ₁ = 2.492(3)	Na-F ₄ -Sr ₁ = 95.3(1)
F ₄ -Sr ₁ = 2.518(2)	Sr ₂ -F ₄ -Sr ₁ = 128.2(1)
⟨F ₄ -Na,Sr⟩ = 2.453	Sr ₂ -F ₄ -Sr ₁ = 98.8(1)
	Sr ₁ -F ₄ -Sr ₁ = 108.3(1)

^a Independent fluorine ion.

From Table III it can be seen that the mean *M*-F distances observed in the polyhedra are in good agreement with the calculated ones with Shannon ionic radii (15). All atoms being in general positions, the cationic polyhedra of Sr and Na are distorted. However, those of Na can be seen as a very distorted octahedra (see angles in Table III and Fig. 2). The eightfold coordination of Sr1 (Fig. 3) can be described as a distorted square antiprism of fluorines whereas the ninefold coordination of Sr2 (Fig. 4) can be described as a monocapped square antiprism. This type of square antiprism, more

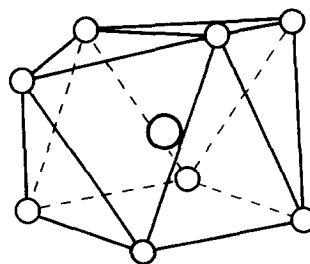


FIG. 3. Sr₁ polyhedron: eightfold coordination.

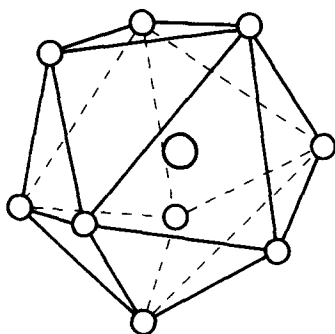


FIG. 4. Sr₂ polyhedron: ninefold coordination.

regular, is frequently found with strontium; it has been already encountered in Sr₁₀Al₂F₂₅Cl (16). However, the main feature of this structure is the existence of two independent fluorines F2 and F4 in addition to those belonging to the CrF₆ octahedron.

Each independent fluorine is surrounded by one Na⁺ and three Sr²⁺ atoms. These tetrahedra build up double chains of formula [F₂Na_{2/2}Sr_{2/2}Sr_{4/4}] = [F₂NaSr₂]_n³ⁿ⁺ by sharing three edges with three other tetrahedra (Fig. 5). In this structure, Na⁺ ions are common to two tetrahedra whereas in the other

structure with [FNaM₃] anti-tetrahedra as Na₂Ca₃Al₂F₁₄ (7) and NaCdAlF₆ (17) the Na ions are terminal. Such double chains have been already encountered in the CsCu₂X₃ (X = Cl, Br, I) (18) and K₃Al₂As₃ (19) phases. This description corresponds to a structural formula [CrF₆][F₂NaSr₂] denoted AB₂X₃, with A = CrF₆, B = F, X = Na, Sr. This notation suggests a comparison with CsCu₂X₃ where Cs⁺ atoms take the place of the CrF₆ octahedron (Fig. 6). Moreover as in CsCu₂Cl₃, CrF₆ octahedra build up a hexagonal close-packing where all octahedral sites are occupied by pairs of tetrahedra which form the double chains [F₂NaSr₂]_n³ⁿ⁺.

Conclusion

This new compound well illustrates the topic on structures containing "independent" fluorine ions (7, 17, 20, 21). Moreover, it also confirms the idea that new topologies in the crystal chemistry of fluorides can be obtained from simple structural formula, here AB₂X₃ where A and B denote an anionic group (complex or not), and X, a cation.

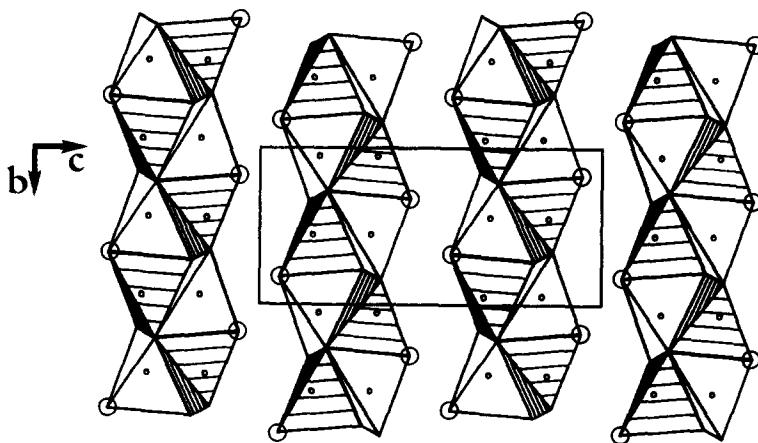


FIG. 5. "Anti-tetrahedra" chains with formula [F₂NaSr₂]_n³ⁿ⁺, (100) projection; (F₂ tetrahedra, shaded; F₄ tetrahedra, unshaded; Na and F_{ind}, large and small circles, respectively).

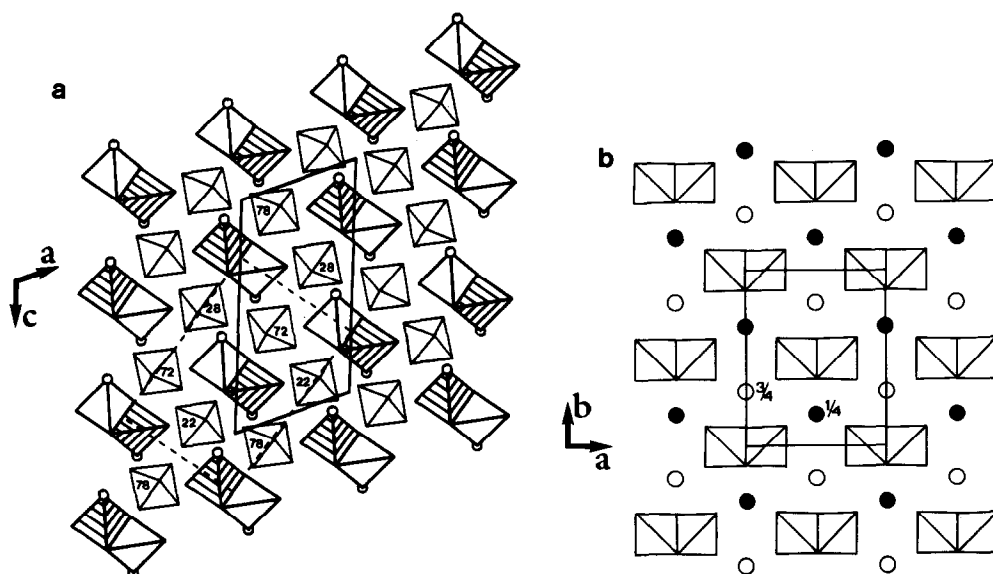


FIG. 6. (a) (010) projection of $\text{NaSr}_2\text{CrF}_8$. Drawn tetrahedra (symbols are defined in Fig. 5) are those centered at $y = 0.44$ or $y = 0.55$ according to the double chain. Numbers indicate the y coordinate of chromium atoms in the octahedra. Dotted lines represent the cell of CsCu_2Cl_3 for structural comparison. (b) CsCu_2Cl_3 structure, (001) projection (black and white circles: Cs^+ atoms).

Acknowledgment

The authors are grateful to Dr. M. Leblanc for his help in X-ray data collection.

References

1. G. COURBION, C. JACOBONI, AND R. DE PAPE, *Acta Crystallogr., Sect. B* **33**, 1405 (1977).
2. G. COURBION, C. JACOBONI, AND R. DE PAPE, *J. Solid State Chem.* **45**, 127 (1982).
3. G. COURBION, R. DE PAPE, J. TEILLET, F. VARET, AND J. PANNETIER, *J. Magn. Magn. Mater.* **42**, 217 (1984).
4. G. COURBION AND M. LEBLANC, *J. Magn. Magn. Mater.* **74**, 158 (1988).
5. G. COURBION, C. JACOBONI, AND P. WOLFERS, *Eur. J. Solid State Inorg. Chem.* **25**, 359 (1988).
6. A. HEMON AND G. COURBION, *J. Solid State Chem.* **84**, 153 (1990).
7. G. COURBION AND G. FERAY, *J. Solid State Chem.* **76**, 426 (1988).
8. J. P. MIRANDAY, C. JACOBONI AND R. DE PAPE, *Rev. Chim. Miner.* **16**, 277 (1979).
9. J. NOUET, C. JACOBONI, G. FERAY, J. Y. GERARD, AND R. DE PAPE, *J. Cryst. Growth* **47**, 699 (1979).
10. G. COURBION, Thesis, Le Mans (1979).
11. A. HEMON AND G. COURBION, to be published.
12. W. CLEGG, *Acta Crystallogr., Sect. A* **37**, 22 (1981).
13. G. SHELDRICK, "SHELX76: A Program for Crystal Structure Determination," University of Cambridge (1976).
14. "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1968).
15. R. D. SHANNON, *Acta Crystallogr., Sect. A* **32**, 751 (1976).
16. A. HEMON AND G. COURBION, *J. Solid State Chem.* **81**, 293 (1989).
17. A. HEMON AND G. COURBION, *J. Solid State Chem.*, in press.
18. G. MEYER, *Z. Anorg. Allg. Chem.* **515**, 127 (1984).
19. G. CORDIER, H. OCHMANN AND H. SCHAFFER, *Rev. Chim. Miner.* **22**, 58 (1985).
20. D. BABEL AND A. TRESSAUD, "Inorganic Solid Fluorides" (P. Hagenmuller, Ed.), p. 77 Academic Press, New York (1985).
21. U. LEUFER AND E. TILLMANN, *Tschermaks Miner. Petr. Mitt.* **27**, 261 (1980).